The relaxation dynamics of a simple glass former confined in a pore

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Abstract

We use molecular dynamics computer simulations to investigate the relaxation dynamics of a binary Lennard-Jones liquid confined in a narrow pore. We find that the average dynamics is strongly influenced by the confinement in that time correlation functions are much more stretched than in the bulk. By investigating the dynamics of the particles as a function of their distance from the wall, we can show that this stretching is due to a strong dependence of the relaxation time on this distance, i.e. that the dynamics is spatially very heterogeneous. In particular we find that the typical relaxation time of the particles close to the wall is orders of magnitude larger than the one of particles in the center of the pore.

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Despite the remarkable progress that has been made in recent years in our understanding of the dynamics of supercooled liquids [1,2] there are still situations in which the nature of this dynamics is very unclear. One example is the behavior of supercooled liquids in restrictive geometries, such as in thin films or in narrow pores [3–5]. The motivation to study the dynamics of fluids in such geometries lies in their importance as catalysts, flow through porous materials, or capillaries in biological systems, to name a few. Apart from their relevance in various applications, this dynamics is also of considerable interest for basic science since it might help us to gain a better understanding of the dynamics of supercooled liquids and the glass transition in the *bulk*, a subject which is, despite the progress mentioned above, still a field of very active research. In particular this type of study might be used to investigate the existence of a diverging length scale in supercooled systems. E.g. investigations of systems that show a conventional ordering phenomena with a growing characteristic length scale, i.e. phase transitions, have shown that, by perturbing the system by means of a wall and by monitoring over which distance this perturbation vanishes, the size of the length scale can be determined. Thus it should be possible to use this approach also in the case of supercooled liquids [6].

Since at low temperatures the modes leading to the relaxation of the system are generally assumed to be very cooperative, one might argue that the confinement will supress such modes and therefore lead to a dynamics which is slower than the one of the bulk. On the other hand one could also think that the interaction between the liquid and the wall of the host material leads to an acceleration of the dynamics, at least close to the walls. In order to decide what is actually happening many experimentalists started to study such systems. Using new nano- and meso scale materials with adjustable pore size, such as Vycor glass and zeolites, and various techniques, such as differential scanning calorimetry, dielectric relaxation measurements, and solvation dynamics, the relaxation dynamics was investigated as a function of pore size, type of liquid and host material, temperature, etc. [7–15]. Surprisingly the obtained results do not give a clear answer at all because for certain materials the glass transition temperature T_g in the confined system is found to be higher than the one of the bulk system [8], whereas in other systems it seems to be lower [9–11]. Sometimes it is also observed that the confinement does not affect the value of T_g at all [12]. However, one has to bear in mind that one of the main problems of these experiments is the proper interpretation of the observed results. Although the topology of the pores can presently be controlled reasonably well [16], the structure of a single pore is never determined exactly. Furthermore it is experimentally not really possible to distinguish between the influence of the fluid-wall interaction, which can be the dominant effect [13], on the one hand from pure confinement effects on the other hand. Therefore it has so far not been possible to obtain a clear picture of the relaxation dynamics in confined systems.

Also computer simulations have been done in order to gain some insight into the dynamics of liquids in restrictive geometries [17–25]. Since in simulations it is easy to control the details of the geometry (size, topology) and also the interaction between confined fluid and host material, this method is well suited to investigate this dynamics. In addition it is possible to measure *directly* all quantities of interest, since at any time the positions and velocities of the particles are known, an advantage of this method which has been made use of extensively in simulations of the bulk [26]. In the past most simulations with restrictive geometries have been done for planar geometries [18–20,24], whereas curved geometries, i.e. tubes or

cavities, have been considered only seldom [21–23]. In the present paper we therefore report the results of a large scale molecular dynamics computer simulation in which we investigated the dynamics of a simple glass former in a narrow pore. In particular we will focus on the dependence of the relaxation dynamics on temperature and the distance from the confining wall.

The system considered is a binary mixture of 80% A and 20% B particles that have the same mass m and which interact via a Lennard-Jones potential of the form $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$, with $\alpha, \beta \in \{A, B\}$ and cut-off radii $r^C_{\alpha\beta} = 2.5 \cdot \sigma_{\alpha\beta}$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. In the following all results will be given in reduced units, i.e. length in units of σ_{AA}, energy in units of ϵ_{AA} and time in units of $(m\sigma^2_{AA}/48\epsilon_{AA})^{1/2}$. For Argon these units correspond to a length of 3.4Å, an energy of $120\mathrm{K}k_B$ and a time of $3 \cdot 10^{-13}$s. The fluid is confined in a cylindrical tube with radius $\rho_T = 5.0$ and below we will compare its properties with the ones in the bulk, using results that have been obtained earlier [27]. In agreement with other computer simulations of confined systems [18,21,24], we find that a *smooth* wall leads to a (in our case strong) layering of the confined liquid, i.e. its structure is very different from the one in the bulk. Since our goal is to investigate the effect of the confinement onto the dynamical properties and not the effect due to a change of structure, a significant change of the structural properties is not acceptable. In order to avoid this latter possibility we chose the wall of the pore to have a liquid-like structure similar to the one of the confined liquid. For this purpose, we equilibrated a large bulk system at a temperature at which it is slightly supercooled, $T = 0.8$, and extracted a cylinder with radius $\rho_T + r^C_{AA}$. Those particles that had a distance ρ from the center of the axis of the cylinder larger than ρ_T were subsequently frozen at their position and constituted the wall particles. The particles for which $\rho < \rho_T$ constituted the fluid and were allowed to continue to move according to Newton's laws using the same Lennard-Jones potential as interaction. With this choice of the wall the static properties of the confined system (density profile, radial distribution function) remain essentially unchanged [25], and therefore the changes in the dynamic properties are only due to the confinement.

The time evolution of the system was calculated by solving the equations of motion with the velocity form of the Verlet algorithm with a time step of 0.01 at high ($T \geq 1.0$) and 0.02 at low ($T \leq 0.8$) temperatures. To improve the statistics of the results we simulated between 8 and 16 independent systems, each containing 1905 fluid particles and about 2300 wall particles. The length of the tube was 20.137 which resulted in an average particle density of 1.2, the same value as used in the earlier simulations of the bulk [27]. The temperatures investigated were $T = 5.0$, 2.0, 1.0, 0.8, 0.7, 0.6, and 0.55. The equilibration was done by coupling the liquid periodically to a stochastic heat bath for a time which was sufficiently long to equilibrate the system. All data presented here were produced during a micro-canonical run at constant energy and volume. During this run we observed that the particles of the fluid are able to enter the wall to some extent. Therefore we defined a "penetration radius" ρ_p as the distance beyond which it is very unlikely to find a particle of the fluid, i.e. the probability is less than 10^{-4}. We found that at low temperatures, $T \leq 0.7$, the value of ρ_p is essentially independent of temperature and that for the A and B particles it is 5.5 ± 0.2 and 6.1 ± 0.2, respectively. Below we will see that this penetration radius, a *static* quantity, is also relevant for the *dynamics* of the system.

A quantity which in the past has been found to be useful to characterize the dynamics of liquids in the bulk is the so-called self intermediate scattering function $F_s(\mathbf{q}, t)$ for wave-vector $\mathbf{q}$, which is related to a density fluctuation $\rho_s(\mathbf{q}, t) = \exp(i\mathbf{q} \cdot \mathbf{r}_j(t))$ by $F_s(\mathbf{q}, t) = \langle \rho_s(\mathbf{q}, t) \rho_s(-\mathbf{q}, 0) \rangle$. (Here $\mathbf{r}_j(t)$ is the position of particle j and $\langle . \rangle$ is the canonical average.) In Fig. 1 we show the time dependence of $F_s(\mathbf{q}, t)$ for all temperatures investigated. The wave-vector is along the axis of the tube and has magnitude $q = 7.18$, which is the location of the main peak in the static structure factor $S(q)$ [25,27]. As it was the case in the bulk [27], the correlation functions show that with decreasing temperature the dynamics of the system slows down rapidly and relaxes at low temperatures in two steps, an effect that is related to the cage-effect. The details of this slowing down, as well as the shape of the correlation function is, however, very different from the bulk behavior. To see this we have included in the figure also three bulk curves for $T = 5.0$, 0.55, and 0.466 (bold dashed lines). We recognize that, whereas the typical relaxation time of the function is basically the same at $T = 5.0$, a decrease of the temperature leads to a slowing down of the dynamics which is much more pronounced in the restricted system than in the bulk system (see the curves for $T = 0.55$). In addition to this also the shape of the curves depends on the geometry in that even at the high temperature $T = 5.0$ the two curves differ since the one for the tube shows a small tail at long times ($t \geq 4$) that is not present in the bulk curve. If the temperature is lowered this tail becomes more pronounced and starts at higher and higher values of $F_s(q, t)$, whereas no such tail is observed in the bulk curves even at the lowest temperatures. Thus the curve for the tube shows a much stronger stretching than the one for the bulk, in agreement with the experimental findings of Refs. [8–10,14].

In order to find the reason for this different dynamical behavior we consider a generalization of the self intermediate scattering function by defining the function $F_s(\mathbf{q}, \rho, t)$ as

$$F_s(\mathbf{q}, \rho, t) = \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \delta(\mathbf{r}_j(0) - \rho) \rangle \quad . \tag{1}$$

Thus this correlation function considers only particles that at time zero had a distance ρ from the central axis of the tube. By investigating the ρ dependence of this correlator it becomes hence possible to understand which particles are moving relatively fast and which ones relatively slow. In Fig. 2 we show the time dependence of $F_s(\mathbf{q}, \rho, t)$ at a low temperature. The direction of the wave-vector is the same as in Fig. 1, i.e. parallel to the axis of the tube. The value ρ_i for the distance ρ is chosen such that the values $(\rho_p - \rho_i)^{-1}$ are spaced equidistantly, where ρ_p is the penetration radius introduced above. (The reason for this choice will become clear below.) Thus the leftmost curve corresponds to $\rho = 0.5$ and the rightmost one to $\rho = 4.96$. From the figure we recognize that the dynamics of the particles close to the center of the tube is similar to the one of the bulk (shown in the figure as bold dashed line). However, for particles that are close to the wall the dynamics is slowed down by several orders of magnitude. We also note that although the time scale of the relaxation function depends strongly on ρ, its *shape*, which could, e.g., be characterized by the value of the Kohlrausch parameter β, seems to be independent of it within the accuracy of our data and that this shape is similar to the one found in the bulk. Since the relaxation curve of the whole system is the weighted sum over the curves for the different ρ, the resulting correlator is much more stretched than the one of the bulk, in agreement with the observation from Fig. 1.

In order to investigate this ρ-dependence of the correlators in more detail we define the

α-relaxation time $\tau(q,\rho,T)$ by the time it takes the correlation function to decay to e^{-1} of its initial value (see the horizontal dashed line in Fig. 2). Such a definition is reasonable since the shape of the correlation function is essentially independent of ρ. In Fig. 3 we plot this ρ-dependence for the different temperatures (curves with open symbols) [28]. For the sake of comparison we have included in the figure also the relaxation times of the system in the bulk (filled symbols). From this graph we see that at high temperatures the relaxation time is independent of ρ, if ρ is not too large, and is the same as in the bulk. Only upon approach to the wall, $\rho \geq 4.0$, $\tau(q,\rho,T)$ starts to increase significantly. With decreasing temperature this crossover distance becomes smaller until at the lowest temperatures the whole system is affected by the slowing down due to the wall. Thus at these temperatures the dynamics of all the particles is slower than the one of the bulk, which can be recognized from the fact that an extrapolation of the curves towards $\rho = 0$ intercepts the vertical line at ρ_{p}^{-1} above the value for the bulk.

From the figure we see that the relaxation times seem to show an apparent divergence upon approaching the wall. We have found that at low temperatures this strong increase can be described well by the functional form $\tau(q,\rho,T) \propto \exp[\Delta_q/(\rho_{\mathrm{p}} - \rho)]$, where ρ_{p} is the penetration radius introduced above, i.e. it is not a fit parameter. To demonstrate the quality of this fit we plot in Fig. 4 the relaxation time in a logarithmic way as a function of $(\rho_{\mathrm{p}} - \rho)^{-1}$ and we see that at low temperatures the resulting fit is indeed very good (bold lines). With increasing temperature we see the expected deviations at small ρ, since there the relaxation times have to approach the bulk values, i.e. they have to become independent of ρ. Nevertheless, even at intermediate and moderately high temperatures the fit describes the data well for large values of ρ. Note that the value of the parameter $\Delta_q = 7.8 \pm 0.2$ is independent of T, at least within the accuracy of our data. Thus close to the wall the only effect of a decrease in temperature is an increase of the prefactor of $\exp[\Delta_q/(\rho_{\mathrm{p}} - \rho)]$. We have found that this temperature dependence is independent of the wave-vector q or the type of particle considered (A or B). At low temperatures we can therefore write the whole temperature and ρ-dependence of the relaxation time as

$$\tau(q,\rho,T) = C(q)f(T)\exp[\Delta_q/(\rho_{\mathrm{p}} - \rho)] \ , \tag{2}$$

where the function $f(T)$ depends strongly on temperature. We have found that this dependence is compatible with an Arrhenius law, in agreement with the experimental findings of Ref. [14], but also with a power-law of the form $(T - T_c)^{-\gamma}$, a functional form suggested by mode-coupling theory [2]. The value of the critical temperature T_c is around 0.39 ± 0.02, i.e. is significantly less than the one found in the bulk which is 0.435 [27]. Also the value for the exponent, $\gamma = 4.7 \pm 0.5$, is much larger than the bulk value 2.35 [27]. Whether or not the dynamics of the particles in the confined geometry can be described by mode-coupling theory as well as it is the case in the bulk is the focus of current investigations.

Before we conclude we briefly comment to what extent these results can be generalized to other systems. It might be expected, e.g., that the strong slowing down of the dynamics close to the wall is related to the fact that the particles of the wall do not move at all, i.e. that they are at zero temperature. However, we have repeated the present calculations also for a system in which the particles in the wall behaved like interacting Einstein oscillators and found that the dynamics is qualitatively the same, i.e. also in this case a strong slowing down close to the wall is found. Furthermore we expect that the same type of slowing

down is observed also in a slit geometry, since the fact that the wall is curved is probably irrelevant.

In summary we can say that by using a wall which does not affect the static properties of the system we have been able to study the effect of the confinement onto the dynamics of a simple liquid in a very clean way. We find that the presence of the wall leads to a strong slowing down of this dynamics and that the time correlation functions are much stronger stretched in the confined system than in the bulk. By measuring the dynamics of the particles as a function of their distance from the wall, we find that the relaxation times show a very strong increase when this distance is small. Therefore we are able to identify the reason why the relaxation of the whole system is so stretched. Note that this increase is a smooth function of the distance from the wall, i.e. we do not see any evidence that the layer of particles closest to the wall is decoupling dynamically from the rest of the liquid, as it has been suggested before [8,9]. In the future it will be of interest to see whether this type of simulation is also useful to identify a growing length scale in supercooled liquids. Work in this direction is currently done by Parisi and coworkers [6].

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[28] Note that we have determined $F_s(\mathbf{q}, \rho, t)$ only for $\rho \geq 0.5$, since for smaller values of ρ the statistics was not satisfactory due to the small phase space.
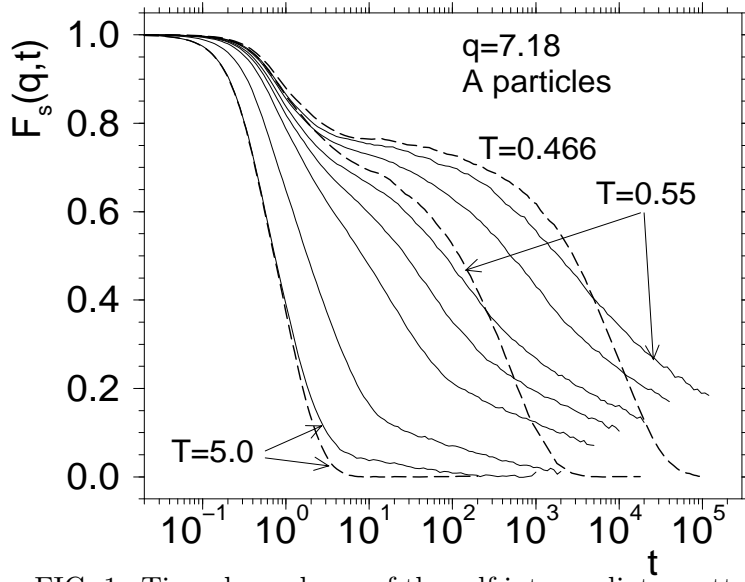
FIG. 1. Time dependence of the self intermediate scattering function for the liquid in the tube (solid curves) for all temperatures investigated and $q = 7.18$ and in the bulk (dashed curves) at selected temperatures and $q = 7.25$.
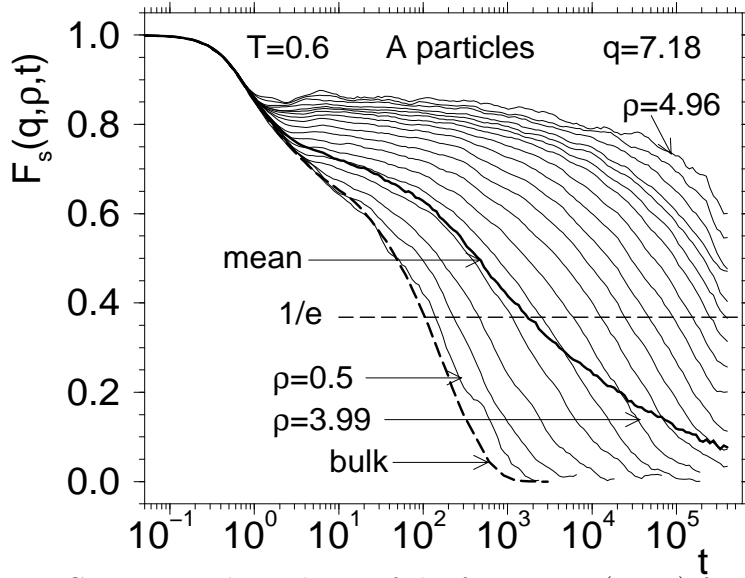

FIG. 2. Time dependence of the function $F_s(q, \rho, t)$ for various distances ρ (thin solid curves). The bold solid curve and the dashed curves are the intermediate scattering function for the whole system and the bulk system, respectively.
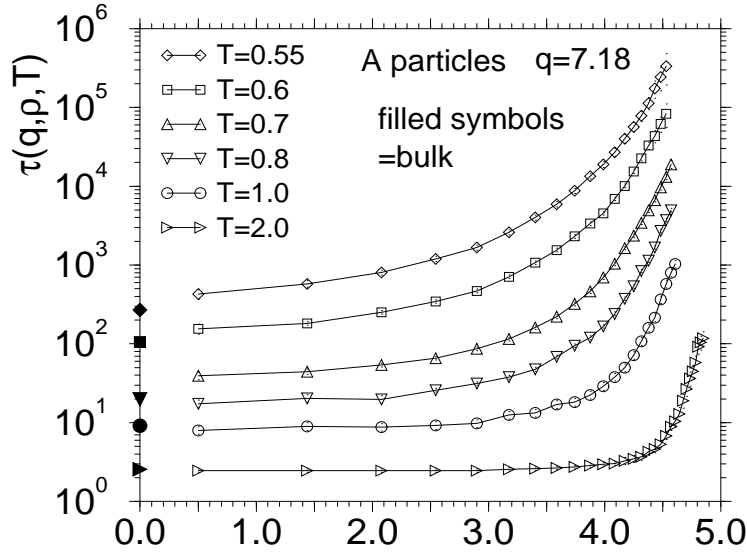
FIG. 3. ρ-dependence of the relaxation time for $T \leq 2.0$ (curves with open symbols with size comparable to the error bars). The single symbols are the relaxation times for the bulk system.
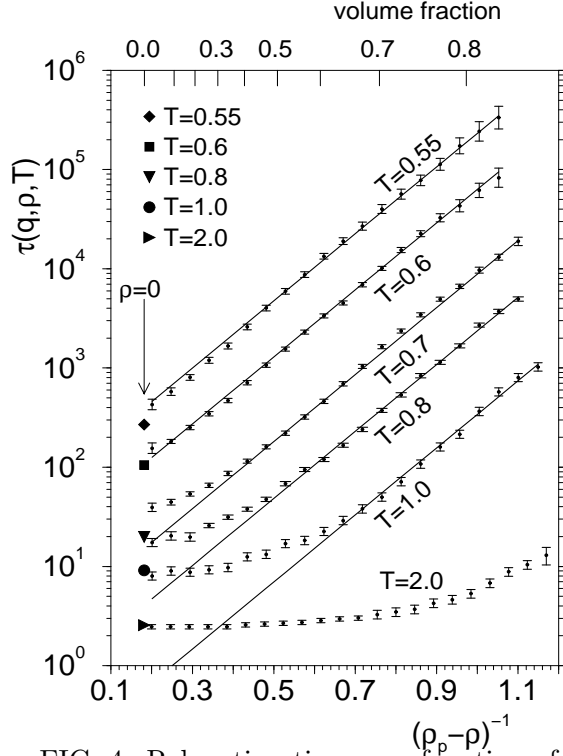

FIG. 4. Relaxation time as a function of $(\rho_p - \rho)^{-1}$, where ρ_p is the penetration radius of the pore. The filled symbols are the relaxation times in the bulk. The straight lines are fits with the functional form of Eq. (2) with Δ_q independent of T.